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Alkoxyalumoxanes $(ROAlO)_n$ – Synthesis and Properties

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Two reaction methods were employed to prepare alumoxanes of general formula $[(RO)AlO]_n$. The first one from Et_3Al, H_2O and ROH [R = CH_3, $(CH_3)_2CH$]; the second one from Et_3Al, ROH [R = $(CH_3)_2CH$, $CH_3(CH_2)_9$] and H_2O. The properties, chemical composition, aggregation and proposed structure of the final products are discussed based on gel permeation chromatography, molecular weight determination and spectroscopic data.

Key words: alumoxanes, alkoxy groups, aggregation

Alumoxanes – compounds formed from the controlled reaction of organoaluminum compounds and water [1–5] are of interest due to their use as catalysts and co-catalysts for the polymerization of organic monomers [6–11] as well as preceramics for alumina [12–15].

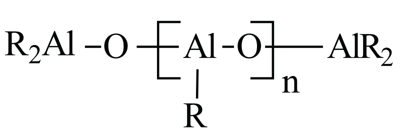
The reaction of the organoaluminum compound – R_3Al with water at 2:1 molar ratio respectively, yields alumoxanes of the general formula $[R_2Al(\mu\text{-}OAlR_2]_n$,

$$2nR_3Al + nH_2O \rightarrow [R_2Al(\mu\text{-}OAlR_2)]_n + 2nRH$$

The reaction at 1:1 molar ratio gives $(RAlO)_n$

$$nR_3Al + nH_2O \rightarrow (RAlO)_n + 2nRH$$

The chemical composition and structure of the final products, especially obtained by the hydrolysis of R_3Al (1:1) depend on reaction conditions, organoaluminum compounds and solvents used as well as isolation methods. For the alumoxanes obtained at 1:1 molar ratio both chain (**1**) and cyclic (**2**) structures have been proposed.



$$R_2Al{-}O{-}\Big[\underset{\displaystyle R}{\underset{|}{Al}}{-}O\Big]_n{-}AlR_2$$

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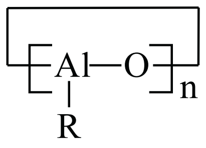

$$\Big[\underset{\displaystyle R}{\underset{|}{Al}}{-}O\Big]_n$$

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The species **1** and **2** can contain from several to tens of [RAlO] units. Kaminsky *et al.* [16] found that methylalumoxane – $(MeAlO)_n$ consists of species containing from 2 to 16 [MeAlO] units. On the basis of spectroscopic evidence and X-ray crystallographic structural determinations Barron showed that alumoxanes of formula $(^tBuAlO)_n$ form three-dimensional clusters [4,5]. The hexa-, octa-, nonametric alumoxane three dimensional cage structures of $[^tBuAl(\mu_3\text{-}O)]$ were found. From the reactions of $(^iBu)_3Al$ and water alumoxanes $(^iBuAlO)_n$; n = 8 and 12, were separated [17] by means of gel permeation chromatography method. Kimura [18] suggests that synthesized by him $[(^iPrO)AlO]_n$ contains more than ten alumoxane units. Pasynkiewicz [3] in comprehensive review discussed the synthesis methods and structures of alumoxanes. Earlier we studied products formed in the (1:1) reaction of tetraethylalumoxane $[Et_2Al(\mu\text{-}OAlEt_2)]_n$ with alcohols [19]. We found the formation of alkoxyalumoxanes $\{Et_2Al[\mu\text{-}OAl(OR)Et]\}_n$ which rearranged into $(Et_2AlOR)_n$ and $(EtAlO)_n$ after cooling reaction solution to law temperature. The stability of the alkoxyalumoxanes obtained depends on kind of OR group. The bulkier the alkoxyl group the milder condition of the rearrangement for studied alumoxanes were found.

In this paper we report the synthesis and properties of alkoxyalumoxanes of general formula $[(RO)AlO]_n$; R = Me, ^{i}Pr, Dec [Dec = $CH_3(CH_2)_9$]. Their structure is discussed based on spectroscopic data, gel permeation chromatography and molecular weight determination.

EXPERIMENTAL

All the reactions were carried out under dry argon due to pyrophoric properties of organoaluminum compounds using Schlenk techniques. Solvents and alcohols were dried by standard methods. The molecular weight of the aluminum compounds studied was determined cryoscopically in benzene or by means of the gel permeation chromatography method. Polystyrene cross-linked with divinylbenzene (3 wt.%) gel was used. Standarization curve of the chromatography column is describe by equation: logM = 3.68–0.0163 V, where M = molecular weight, V = eluent volume. 0.5 g samples of the studied aluminum compounds were introduced on the column and eluted with toluene (100 ml). 5 ml toluene samples were collected. The content of the aluminum was checked in each sample and then measured by standard analytical method. NMR spectra were run on a Varian VXR-300 spectrometer.

Synthesis of $[(MeO)AlO]_n$ ***4***, $[(^iPrO)AlO]_n$ ***5*** *– method* ***A***. H_2O (0.24 ml, 13.2 mmol) was added (15 min) to a stirred solution of Et_3Al (1.5 g, 13.2 mmol) in toluene (20 ml) cooled to 0°C. The mixture was then stirred further at ambient temperature for 2 h and 6 h at 50°C. Volume of ethane evolved: found: 550 ml; calcd.: 591 ml. The reaction mixture was then cooled to –30°C and an appropriate alcohol (MeOH, 0.42 g; ^{i}PrOH, 0.79 g; 13.2 mmol) was added slowly (15 min). The mixture was stirred (1 h) at room temperature and (8 h) at 50°C. Toluene was evaporated off in vacuo to give a white amorphous solid. Volume of ethane evolved; found: 281, 263, respectively, calcd.: 295 ml.

Synthesis of Et_2AlO^iPr ***6***. ^{i}PrOH (0.79 g, 13.2 mmol) was added (0.5 h) to a stirred solution of Et_3Al (1.5 g, 13.2 mmol) in toluene (20 ml) cooled to –30°C. The reaction mixture was warmed up to ambient temperature and stirred for 3 h. During the reaction ethane evolved. Toluene was evaporated off in vacuo to give a colorless liquid of (**6**) (yield 1.88 g, 99%). Anal. found: Et, 39.80; Al, 19.01; M_w (cryoscopically in benzene) 295 (n = 2.05). $C_7H_{17}OAl$ calc.: Et, 40.27; Al, 18.71%; M_w = 144. ^1H NMR (THF-d_8, –60°C): δ 0.08 (q, 4H, $CH_3C\mathit{H}_2$), 1.04 (t, 6H, $C\mathit{H}_3CH_2$), 1.31 (d, 6H, CH_3), 3.98 (sep. 1H, CH). ^{27}Al NMR (C_6D_6) 131 ppm.

Synthesis of Et$_2$AlODec 7. DecOH (2.77 g, 17.5 mmol) was added (0.5 h) to a stirred solution of Et_3Al (2 g, 17.5 mmol) in toluene (20 ml) cooled to –10°C. The reaction mixture was warmed up to ambient temperature and stirred for 12 h. During the reaction ethane evolved. Toluene was removed in vacuo to give a thick colorless liquid of **7** (yield 4.15 g, 98%). Anal. found: Et, 23.65; Al, 11.21; M_w (cryoscopically in benzene) 579 (n = 2.39). $C_{14}H_{31}OAl$ calcd.; Et, 23.96; Al, 11.13%; $M_w = 242$. ^1H NMR (C_6D_6): δ 0.32 (m, 4H, CH_3CH_2), 1.02 [t, 3H, $CH_3(CH_2)_9$], 1.35 [m, 22H, $CH_3(CH_2)_8CH_2$ and CH_3CH_2], 3.80 [m, 2H, $CH_3(CH_2)_8CH_2$] ppm. ^{27}Al NMR (C_6D_6) 129 ppm.

Synthesis of [(^{i}PrO)AlO]$_n$ ***5*** *– method* ***B****.* H_2O (0.27 g, 15 mmol) was added (1 h) to Et_2AlO^iPr (2.16 g, 15 mmol) in toluene (50 ml) cooled to 0°C. The mixture was allowed to warm up to room temperature (1 h) and then the reaction was carried out at 50°C (8 h). During the reaction ethane evolved. Toluene was evaporated off in vacuo to give a white solid **5** (yield 1.45 g, 95%). Anal. found: Et, 3.88; Al, 25.73, M_w (cryoscopically in benzene) 595 (n = 5.83). $C_3H_7O_2Al$ calc.: Et, 0; Al 26.43 %; $M_w = 102$. ^1H NMR (C_6D_6): δ 1.50 (bs, CH_3), 4.44 (bs, CH) ppm. ^{27}Al NMR (C_6D_6): δ 45, 105 ppm.

Synthesis of [(DecO)AlO]$_n$ ***8*** *– method* ***B****.* H_2O (0.27 g, 15 mmol) was added (1 h) to a stirred solution of $Et_2AlODec$ **7** (3.63 g, 15 mmol) in toluene (50 ml) cooled to 0°C. The reaction mixture was warmed up to ambient temperature and stirred (12 h). During the reaction ethane evolved. The solvent was evaporated off in vacuo to give a thick colorless liquid of (**8**) (yield 2.94 g, 98%). Anal. found: Et, 0; Al, 13.39. $C_{10}H_{21}O_2Al$ calc.: Et, 0; Al, 13.47%; $M_w = 200$. ^1H NMR (C_6D_6): δ 1.10 (bs, CH_3), 1.52 (bs, $(CH_2)_8$), 4.33 (bs, CH_2O) ppm. ^{27}Al NMR (C_6D_6): δ 4, 39, 112 ppm.

RESULTS AND DISCUSSION

To obtain the alumoxanes of general formula $[(RO)AlO]_n$ we applied two methods of their synthesis:
A – from Et_3Al with water and then alcohol

$$nEt_3Al + nH_2O \rightarrow \underset{\mathbf{3}}{(EtAlO)_n} + 2nEtH \tag{1}$$

The $(EtAlO)_n$ **3** obtained according to reaction (1) was then reacted with methanol and isopropanol (eq. 2) to yield $[(MeO)AlO]_n$ **4**, and $[(^iPrO)AlO]_n$ **5**, respectively.

$$(EtAlO)_n + \underset{R = Me,\ ^iPr}{nROH} \rightarrow \underset{\mathbf{4,\ 5}}{[(RO)AlO]_n} + nEtH \tag{2}$$

B – from Et_3Al with alcohol and then water

In the first step of method **B**, Et_2AlOPr^i **6** and $Et_2AlODec$ **7**, where Dec = $CH_3(CH_2)_9$, were obtained from the reaction of Et_3Al with isopropanol and decanol, respectively according to eq. 3

$$Et_3Al + \underset{R = ^iPr,\ Dec}{ROH} \rightarrow \underset{\mathbf{6,\ 7}}{Et_2AlOR} + EtH \tag{3}$$

Compounds **6**, **7** were then reacted with water (eq. 4) to yield $[(^iPrO)AlO]_n$ **5** and $[(DecO)AlO]_n$ **8**, respectively.

$$n\underset{\mathbf{6,\ 7}}{Et_2AlOR} + nH_2O \rightarrow \underset{\mathbf{5,\ 8}}{[(RO)AlO]_n} + 2nEtH \tag{4}$$

Method ***A***. We found that the synthesis of alumoxanes according to method **A** (R = Me, ^{i}Pr) results in the final products **4** and **5** very poorly soluble in toluene, THF and CH_2Cl_2. The hydrolysis of Et_3Al (eq. 1) was carried out in toluene or THF at 0°C, and then after dropping a water the reaction mixture was warmed up to 50°C. The reaction was continued at this temperature until ethane stopped evolving. The reaction, however, does not proceed quantitatively. The volume of ethane evolved was found to be 90–95% of the theoretical value. The ethylalumoxane **3** synthesized in the first stage of method **A** (eq. 1) was then reacted with methanol or isopropanol (eq. 2). The alcohol was added dropwise to a cooled ethylalumoxane solution (–30°C), the temperature was raised slowly to 50°C and the reaction was continued until ethane stopped evolving. Again 90–95% of the theoretical value of ethane was found to evolve. The volumetric analysis of hydrolyzable ethyl groups show that the reaction products **4** and **5** still contained 2–4 wt % of ethyl groups bonded to aluminum. The alumoxanes **4** and **5** are white amorphous solids. However, due to their very poor solubilities they have not been studied further.

It seems that the reason of poor solubility of the alumoxanes obtained according to method **A** is the formation of complex species in the first step of their synthesis (eq. 1). It is well known from literature that the ethylalumoxane $(EtAlO)_n$ is a mixture of aggregates of an average association degree n = 10–23 [20,21]. Because the reaction of Et_3Al with water at 1:1 molar ratio does not proceed quantitatively the compound **3** formed (eq. 1) contains an unreacted hydroxyl and ethyl groups. The inactivity of the groups in alumoxane aggregate **3** probably results from steric hindrances. The addition of alcohol to ethylalumoxane leads to a decrease of the alumoxane association degree due to replaceing donor-acceptor bonds of oxygen with aluminum in **3** by alcohol oxygen-aluminum ones. This way the ethyl and remaining hydroxyl groups become available for reaction giving not only cyclic/chain alumoxanes of the general formula $[(RO)AlO]_n$ but cross-linked species as well.

Method ***B****. Synthesis and characterization of* $Et_2AlO^{i}Pr$ ***6****,* $Et_2AlODec$ *7.* Diethylaluminum alkoxides **6**, **7** were prepared from the 1:1 reaction of Et_3Al with ^{i}PrOH or DecOH (eq. 3). The reaction of the alcohols used with Et_3Al proceeds quantitatively. The alkoxide derivatives formed are thick colorless liquids. The compounds **6, 7** were characterized by elemental analysis, ^{1}H NMR, ^{27}Al NMR spectroscopy and molecular weight measurements (see Experimental).

The molecular weight measurements of the alkoxylauminum compounds **6** and **7** were determined cryoscopically in benzene. $Et_2AlO^{i}Pr$ **6** was found to be a dimer; n = 2.05, and $Et_2AlODec$ **7** a mixture of dimer and trimer forms, n = 2.39. Aluminum atoms in both compounds are four-coordinate. ^{27}Al NMR spectra of **6** and **7** show signals at 131 and 129 ppm, respectively. The cryoscopic molecular weight determination for the decyloxyaluminum derivative **7** was confirmed by the gel permeation chromatography method. On polystyrene cross-linked with divinylbenzene gel using toluene as eluent compound **7** was separated into three phases. The molecular weight of the first phase (13 wt %) corresponds to a trimer – found: 667±33; $Et_2AlODec$ calcd: 242; the second one (33 wt %) corresponds to a dimer-trimer mixture 553±28 and the third one (52 wt %) – 458±23 to a dimer.

[(^{i}PrO)AlO])$_n$ **5** *from the reaction of* Et_2AlOPr^i *with water.* The alkoxyaluminum compounds **6** and **7** obtained according to eq. 3 were reacted with an equimolar amount of water (eq. 4). We found that the degree of hydrolysis depends on the organoaluminum compound used. In the reaction of Et_2AlO^iPr with water the volume of ethane evolved was 85–90% of the theoretical value. Product **5** formed from reaction (4) is a white powder well soluble in toluene, THF and CH_2Cl_2. The resulting product contains AlO–^{i}Pr, Al–OH, Al–Et and Al–O–Al bonds. IR spectra of **5** show an Al–OH broad band at 3200–3400 cm^{-1}, C–O bands at 1030 and 1070 cm^{-1} of an isopropyl group bonded to an aluminum atom and an Al–O–Al band at 840 cm^{-1}. The ^{1}H NMR spectrum shows two broad signals of CH_3 and CH protons of isopropoxy groups at 1.50 and 4.44 ppm, respectively. Signals of ethyl groups bonded to aluminum atoms were not noted in the spectrum. Volumetric analysis of hydrolyzable ethyl groups show, however, that the product **5** contains an Et–Al bonding. During the analysis ethane evolved. The average Al:Et molar ratio was found to be 6:1. ^{27}Al NMR spectra of product **5** show broad signals at 105 and 45 ppm indicating four- and five-coordinate aluminum atoms.

The reaction of Et_2AlO^iPr with water was repeated several times and the molecular weight 532–628 of the resulting product was determined cryoscopically. The values of the molecular weight found correspond to aggregates containing *ca.* 5–6 alumoxane [Al–O] units. The structure of the alumoxane aggregates **5** is believed to be three-dimensional. The aggregates involve four and five coordinate aluminum atoms. Since in the reaction studied the hydrolysis of Et–Al bonds is not quantitative, some alumoxane aggregates contain, besides AlO–^{i}Pr bonding, also Et and/or OH substituents at aluminum.

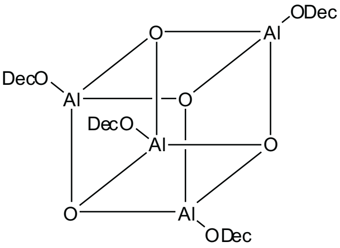
[(DecO)AlO]$_n$ **8** *from the reaction of* $Et_2AlODec$ *with water.* The reaction of $Et_2AlODec$ **7** with water (1:1) proceeds quantitatively (eq. 4). In the resulting product Et–Al bonds were not found in ^{1}H NMR spectra as well as by volumetric analysis method. The removal of the solvent from post-reaction mixture of **8** gives a sticky, colorless solid well soluble in common organic solvents: toluene, CH_2Cl_2, THF. In IR spectra of product **8** a band of hydroxyl groups at 3200–3400 cm^{-1} was not noted. ^{1}H NMR spectra show three broad signals of decyloxy substituents at the expected field range (see Experimental).

The sticky solid of **8** was dissolved in benzene and the molecular weight was determined by cryoscopic molecular weight method.The molecular weight was found to be > 5000 which gives an association degree n > 25. When, however, the synthesis of **8** was carried out in benzene and the benzene solution of the alumoxane was used directly for molecular weight measurements an association degree n = 3.6 found. The results show that removal of the solvent from the reaction mixture leads to an increase in the association degree of alumoxane **8**.

The cryoscopical data are consistent with results obtained by means of the gel permeation chromatography method. When the post-reaction toluene solution of alumoxane **8** was used directly after synthesis without distilling off the solvent, the compound separated on a chromatographic column into three fractions. The molecular weight of the first fraction was found to be 805±43; 26 wt % (calcd. 200); the second one 667±33; 52 wt % and the third one 553±27; 18 wt %. The results show that the first fraction contains a tetramer of the studied alumoxane, the second one a tetramer–trimer mixture, and the third one mainly a trimer.

For the alumoxane **8** but after removal of the solvent in vacuum, dissolving again in toluene, and introducing on a chromatographic column one fraction was found only. This fraction (98 wt %) appears at the beginning of elution, out of the limit of column separation. It indicates that the molecular weight of **8** is above 1700–1800 and confirm results obtained cryoscopically.

Spectroscopic and elemental analysis data indicate that cyclic alumoxane species of **8** are formed from 1:1 reaction of $Et_2AlODec$ and water. The molecular weight measurement show that the studied alumoxane aggregates contain three and four [(DecO)AlO] units. For an alumoxane tetramer we postulate structure **Y** shown below:



Y

Removal of the solvent from the post-reaction mixture gives highly associated alumoxane aggregates containing four- five- and six-coordinate aluminum atoms. The ^{27}Al NMR spectra of high molecular weight alumoxane aggregate **8** show signals at 4, 39, 112 ppm, respectively.

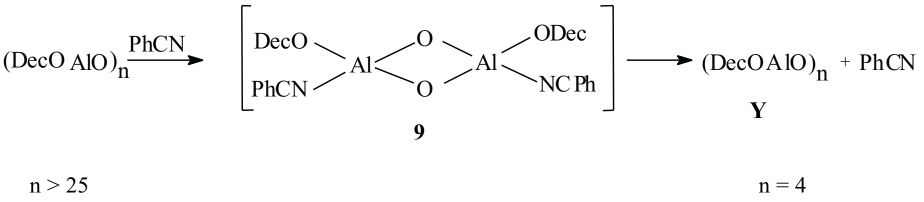
We found that alumoxane **8** does not form stable donor–acceptor complexes with benzonitrile. In IR spectra of a highly associated alumoxane (n > 25) – benzonitrile mixture (1:1) only a free benzonitrile band at 2230 cm^{-1} of a $C\equiv N$ group is present.

Though no stable complexes of alumoxane **8** with PhCN were found to be formed, however, in the presence of the electron donor a decrease in the association degree of alumoxane aggregates takes place. Mixtures of highly associated alumoxane (n > 25) with PhCN at 1:1 and 1:2 molar ratio, respectively, were prepared and their average molecular weight was measured cryoscopically. The calculated molecular weight of the alumoxane from each measurement was found to be 740, n = 3.7.

The results show that PhCN serves as a Lewis base forming unstable donor-acceptor bonds with aluminum atoms. The disruption of Al–O–Al and/or Al–O(Dec)–Al bridge bonds takes place then and the smallest alumoxane species appear. The association degree n = 3.7 of the alumoxane found indicates that a trimer and tetramer are formed. Distilling off PhCN leads again to the formation of highly associated alumoxane aggregates (n > 25).

The change in association degree from thermodynamically favoured Et_2AlOMe trimer to dimer in the presence of benzonitrile we observed earlier [22]. IR spectra of the studied Et_2AlOMe with benzonitrile mixture show band a free benzonitrile only.

It can assume that the one of reaction way leading to smallest alumoxane aggregates when benzonitrile added is for example the formation of weak alumoxane–benzonitril complexes **9** (eq. 5)



9

Y

(5)

The complex **9** transforms yelding tetramer **Y** and free benzonitrile.

As it has been mentioned earlier, alumoxane **8** which is used directly after synthesis, without removal of the reaction solvent, can be separated by means of the gel permeation chromatography method into three fractions of average molecular weight 805 (i); 667 (ii) and 553 (iii), respectively. Removal of the eluent under vacuum from each fraction leads to the formation of high molecular weight alumoxane aggregates (n > 25). To each alumoxane fraction, after removal of the solvent, PhCN (1:1) was added; the average molecular weight of the mixture was measured cryoscopically and the molecular weight of the alumoxane was calculated. The molecular weight of alumoxane **8** was found to be for fraction (i) – 809, n = 4.04; (ii) – 680, n = 3.4; (iii) – 624, n = 3.12. IR spectra of the mixtures studied did not show complexed PhCN. The results confirmed that alumoxane **8** consists of trimer and tetramer species.

CONCLUSIONS

We have found that solubility of the synthesized alumoxanes of general formula $[(RO)AlO]_n$ depends on employed method (**A** or **B**) of their synthesis. Method **B** gives final products soluble in toluene, THF, CH_2Cl_2. Method **A** leads to the formation of insoluble alumoxanes **5**, **6**.

We found that the $[(^iPrO)AlO]_n$ **5** obtained according to method **B** formed species containing *ca.* 5–6 alumoxanes $[(^iPrO)AlO]$ units. The hydrolysis of Et_2AlO^iPr (1:1) does not proceed quantitatively. The final product contains beside Al–O^{i}Pr bonding also Et and OH substituents at aluminum atoms.

The hydrolysis of $Et_2AlODec$ (1:1) was found to be quantitative giving decyloxyalumoxane species **8**. The species contain 3 and 4 [(DecO)AlO] units. We found that the trimeric and tetrameric decyloxyalumoxane species can associate forming high molecular weight alumoxane aggregates; n > 25. The highly associated decyloxyalumoxane aggregates are stable in aromatic solvent used. In the presence of PhCN the large alumoxane aggregates dissociate to trimer and tetramer. Though no stable complexes of the decyloxyalumoxane with PhCN were found the results show that PhCN serves as a weak Lewis base.

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